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(54) An atmospheric plasma reaction method and a device therefor.

(57) This invention provides an atmospheric plasma reaction method characterized by introducing a mixed gas of rare gas and reactive gas into a reaction vessel having a dielectric-coated electrode wherein the surface of two or more electrodes located parallel therewith are provided with solid dielectrics, exciting said mixed gas of gases with plasma at atmospheric pressure, then transporting the active species to the downstream of the plasma and treating the surface of a substrate.

This invention also provides an atmospheric plasma reaction device.

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AN ATMOSPHERIC PLASMA REACTION METHOD AND A DEVICE THEREFOR

The present invention relates to an atmospheric plasma reaction method and the device therefor. More particularly, this invention relates to an atmospheric plasma reaction method and the device therefor wherein stable glow discharge plasma is caused to generate under atmospheric pressure, and also the active species generated by this atmospheric plasma is transported to the downstream for treating the surface and/or forming a thin film on a large-size substrate.

Conventionally, a film-forming or surface treatment method with low pressure glow discharge plasma has been widely known, and has found extensive applications in various industrial fields. As the surface treatment method with low-pressure glow discharge plasma, the so-called plasma etching method that an etching and a thin film formation are made by the plasmatization of reactive gases including halogen atoms and silicon atoms, and the deposit method are known.

Such plasma etching method and deposit method include etching of silicon and oxidated silicon film with Freon gas and other carbonfluoride plasma in a vacuum container, and depositing of amorphas silicon film, oxidated silicon film or nitride silicon film onto a silicon substrate or glass substrate by plasma-exciting silane gas or a mixed gas of oxygen or ammonia gas therewith.

However, the surface treatment methods of low-pressure glow discharge plasma as has conventionally been known, use reactions under vacuum of some $1x10^{-2}$ - 1 Torr, and hence a device and equipment for forming these low-pressure conditions were required. It was also difficult to treat a large-area substrate and the production cost was inevitably high.

One of the inventors to the present invention has already proposed a plasma reaction method for plasma exciting monomer gas introduced in a mixed gas with rare gas under atmospheric pressure and treating the surface of a substrate. He has put this method into application, achieving a surface with superb characteristics and functions. However, there was a limit to the treatment of surface even by this method, and particularly in the case where a gas is metal or alloy, are discharge occurred under atmospheric pressure, making the treatment difficult. In addition, the treatment area depends on the area of an electrode, and hence it was difficult to treat a large area.

The present invention has been made considering the aforestated circumstances, and is a further expansion of the method already proposed. It has an objective of providing an atmospheric plasma reaction method and the device therefor which can give plasma with reaction activity and stability under atmospheric pressure, without any arc discharge occurring even in the case where the substrate is a metal or an alloy or it is a large area substrate.

This invention provides an atmospheric plasma reaction method characterized by introducing a mixed gas of rare gas and reactive gas into a reaction vessel having a dielectric coated electrode wherein the surface of two or more electrodes located parallel ther with are provided with solid dielectrics, exciting said mixed gas of gases with plasma at atmospheric pressure, then transporting the active species to the downstream of the plasma and treating the surface of a substrate.

This invention also provides an atmospheric plasma reaction device comprising a gas introducing unit for intoducing mixed gas of rare gas and reactive gas into a reactive vessel, a atmospheric plasma generation unit wherein a dielectric-coated electrode where a solid dielectric is produced on the surfaces of two or more electrodes located parallel therewith is provided vertical to the substrate, and a surface-treatment unit for treating the surface of the substrate downstream of the plasma-generating region at the atmospheric plasma generation unit.

Fig. 1 is a sectional view illustrating one of the embodiments of an atmosphere plasma reaction device of this invention.

Fig. 2 is a perspective view illustrating the structure of a dielectric-coated electrode.

Fig. 3 is a perspective view illustrating another embodiment of an atmosphere plasma reaction device of this invention.

Figs. 4 and 5 are correlation drawings which show the relationships between the etching speed of Si and SiO_2 at substrate temperatures of 100°C and 20°C and the concentration of O_2 in CF_4.

Fig. 6 is a correlation drawing showing the relationships between the etching speeds of Si and SiO_2 and substrate temperatures.

Fig. 7 is a correlation drawing showing the relationships between the etching speeds of Si and SiO_2 and the location of the substrates.

In an atmospheric plasma reaction method according to the present invention and the device therefor, a mixed gas of rare gas with reactive gas is used, and dielectric-coated electrodes with which a solid dielectric is provided are located perpendicular to a substrate, and a surface treatment portion for supporting a substrate and treating the surface thereof is provided downstream of the plasma-generating portion of an atmospheric plasma generating unit making possible stable glow discharge and the surface-treatment of a large-area substrate. Even where the substrates a metal or an alloy, stable glow discharge can be obtained, and where it is a large-area substrate,

the surface treatment can be ensured.

Detailed descriptions will be made as to the embodiments of this invention while referring to the drawings.

Fig. 1 is a sectional view of one of the embodiments illustrating an atmospheric plasma reaction device of this invention.

As shown in this example, the device according to the present invention comprises a gas introducing unit (3) for introducing mixed gas (1) of rare gas and reactive gas into a rection vessel (2) consisting of Teflon plate and which is kept at atmospheric pressure, an atmospheric plasma generating unit (8) wherein a dielectric-coated electrodes (6) with a solid dielectric (5) provided on the surfaces of two or more electrodes (4) are located parallel with each other is located perpendicular to a substrate (7) and a surface treatment unit (9) which supports the substrate (7) downstream of the plasma generating portion of that atmospheric plasma generating unit (8) and treats the surface thereof with the active specifies generated.

Generally, glow discharge will not occur readily under atmospheric conditions. Arc discharge is occured by applying high voltage, and hence it becomes difficult to perform the surface treatment of a substrate.

In this invention, however, glow discharge under atmospheric pressures is made possible by using a mixed gas (1) of reactive gas with rare gas, locating dielectric-coated electrodes (6) with solid dielectrics (4) provided with electrodes (5) perpendicular to a substrate (7), and providing a surface treatment unit (9) for supporting the substrate (7) downstream of the plasma generating region of the atmosphere plasma generating unit (8).

Even when the substrate (7) is a metal or an alloy, a stable glow discharge can be obtained, and even when it is a large-area plate, the surface treatment of said substrate can be ensured. There is no need to say that when the substrate is of ceramics, glass, plastic and rubber, stable glow discharge is ensured and a substrate of large area can be subject to surface treatment.

Fig. 2 illustrates the structure of dielectric coated electrodes (6) located in an atmosphere plasma generating unit (8) which excites a mixed gas (1) of rare gas and reactive gas under atmospheric pressures.

In this example, a total of four electrodes parallel plate ground electrodes (41) two pairs each provided parallel with each other are used. A high-frequency electric field is applied from a high-frequency power suply (11) to the high-frequency electrodes (42) via a matching device (10). The both sides of each of these electrodes (41)(42) are provided with a solid dielectric field (5). The materials of the solid dielectric field (5) include glass, ceramics, plastic and other heat-resistant materials.

A mixed gas of rare gas and reactive gas is excited with glow discharge using such dielectric-coated electrodes (6), generating high-energy plasma. The formation of this plasma is provided by the application of high voltage from the high-frequency power supply (11). The voltage applied at that time may be arbitrary depending on the property of the surface of the substrate and the time for which the surface is treated.

There is no special limitation to the number of electrodes, but any number of two or more is acceptable. Nor is there any specific limitation to the materials of the electrodes (41)(42). Stainless steel and other given material may be used.

As illustrated in Fig. 1, a mixed gas (1) of rare gas and reactive gas is introduced into a reaction vessel (2) through a gas introducing port (12) provided on the reaction vesel (2), passes through a space (13) and is dispersed evenly at an atmosphere plasma generating unit (8). Gases from a reaction product, unracted portion of reactive gas and rare gas are discharged via an exhaust port (15).

To obtain more stable plasma at atmospheric pressure, it is preferred to disperse and supply a mixed gas (1) of rare gas and reactive gas to the plasma generating region in the vicinity of dielectric-coated electrodes (6). For this reason, in this example, a multi-port plate (16) is also provided.

At a substrate support (14), a temperature sensor (17) which measures the temperature of the substrate (7) of a thermocouple, a heater (18) for heating the substrate (7), and a water-cooled pipe (19) for cooling the substrate (7), are also provided. These means may be arbitrarily provided.

There is no specific limitation to a mixed gas (1), but as rare gas to be used, He, Ne and Ar can used singularly or in combination with other substances. To prevent arc discharge and provide stable glow discharge, it is preferred to use He, a gas with light mass. For reactive gases to be introduced in combination with rare gases, silicon hydrogases such as silane (SiH_4) and disilane (Si_2H_6) or halogenated hydrocarbon including CF_4, C_2F_5, CHF_3 or SF_5 and hydrocarbons with or without other functional groups may be used arbitrarily. Reactive gases with multiple species can be mixed and used for that application. Furthermore, depending on the reactive gases to be used, halogen, oxygen, and hydrogen may be added to the mixed gas to accelerate a reaction. There is no specific limitation to the mixing ratio of rare gas with reactive gas, but it is preferred to make the density of rare gas about 65% or higher, especially 90% or higher.

When these gases used for a reaction are released into the atmosphere, there are some cases where they will cause safety problems including fire and undesirble effects upon the human body. In order to avoid this cases, it becomes necessary to dotoxify these gases. Since the gases such as He are expen-

sive, it is prefered to collect them for reuse. Given these, the device of this invention can be covered with a separate container (21) from the reaction vessel (2) which is used to isolate a plasma reaction system from atmosphere. Using a pump and other appropriate exhaust means connected to the isolation container (21), the pressure inside can be reduced to approx. 0.5 to 0.1 atmospheric pressure. The discharge mechanism for this is identical to that under atmospheric pressure.

According to the type and reaction conditions of reactive gases to be used, plasma polymer film, deposit film, plasma treatment film or plasma etching surface can be obtained.

Fig. 3 is a perspective diagram of another example of the atmosphere plasma reaction device of this invention.

In this example, a pair of dielectric-coated electrodes (6) with a solid dielectric (5) provided on one of the sides of the electrodes (4) and longer in the cross direction of a substrate (20) are provided inside a convex reaction vessel (2), so that the substrate (20) is scanned in the directions of an arrow (x) and/or an arrow (y). This ensures that if the substrate (20) is a large-area substrate, the surface can be treated. When this device is used for surface treatment, it is preferrd to scan the substrate (20) in both directions of the arrows (x)(y) to provide more evenly treated surface.

In this case also, to prevent the gases from dispersing into the atmosphere, the whole device can be covered by an isolation container different from the reaction vessel (2). With an appropriate exhaust means such as a pump, the internal pressure can be reduced to approx. 0.5 to 0.1 atmospheric pressure. The discharge mechanism for this operation is similar to that under atmospheric pressure.

Now, Description will be made as to the specific examples of surface treatment.

Treamtment Example 1

In a device as descried in Fig. 1 wherein four plate electrodes with a shape of square having a 30 mm side are used, and glass plate-coated electrodes, located parallel with each other in a clearance of 4 mm, were provided at an atmosphere plasma generating portion, 1 cm^2 single crystal silicon (100) and thermally oxidated film were provided 1 cm apart from the bottom of the dielectric-coated electrodes. These substances were heated to 100°C to vary the concentration of O_2 into CF_4 for plasma etching. The total flow of $CF_4 + O_2$ was kept constant at 25 sccm, and the flow rate of He at 4×10^3 sccm. A high-frequency power at 13.56 MH_2 was set at 70 V. The result is show in Fig. 4.

The single crystal silicon and thermal treated film were subject to etching. The etching speed was approx. 2.5 heat $(CF_4 \div O_2)/O_2$ ratio, i.e., it was confirmed that when CF_4 was approx. 30 cc and O_2 was some 70 cc, the silicon (S1) and the oxidated film (SiO_2) attained the maximum etching speed.

During the etching operation, no arc discharge occured, and glow discharge ocurred under stable atmospheric pressures, giving highly active plasma.

Temperature Example 2

Under the same condition as in Example 1, except for setting the temperature of the substrate at 20°C, a single crystal silicon and thermally oxidated film were subject to etching. The result is show in in Fig. 5. As is shown by a comparison with Fig. 4, it was found that the etching speed of the silicon (Si) does not change greatly with substrate temperatures, but that the etching speed of oxidated film (SiO_2) decreases substantially, improving the selection ratio of Si/SiO_2 more than 15 times.

In this case also, no arc discharge occurred and glow discharge occurred under stable atmospheric pressures, giving highly active plasma.

Treatment Example 3

Keeping the flowrate ration $(CF_4 \div O_2)/O_2$ at 3 and varying substrate temperatures, the etching speed of a single crystal silicon and thermally oxidated film were observed. The result is indicate in Fig. 6.

The single crystal silicon and thermally oxidated film was subject to etching. As is evident from Fig. 6, it was confirmed that the selection ratio of Si/SiO_2 became enormously larger as the substrate was cooled.

In this case also, during the etching operation, glow discharge occurred, giving highly active plasma. No arc discharge occurred.

Treatment Example 4

Under similar conditions as in Example 3 and varying the location of the substrates with regard to dielectric-coated electrodes, the etching speed of the silicon (Si) and thermally oxidated film (SiO_2) was observed. The location of the substrate in this case was further apart from those in Example 1 to 3.

It was determined that the etching speeds of both the silicon (Si) and thermally oxidated film (SiO_2) decrease as they are more distant from the dielectric-coated electrodes, but that an effective etching speed was achievable even when those substrates are 3 cm distant from the electrodes.

The present invention is not limited to the above examples. Various configurations can be realized depending on the geometry, size and material of a reaction vessel, the construction and structure of a dielectric-coated electrode, the type and flowrate of

rare gas and reactive gas, the quantity of applied power, substrate temperature, and the location and distance of the substrate from the dielectric-coated electrodes.

When the pressure inside the container is to be reduced for the exhaust and disposal of reactive gas and reaction production and the collection of He and other rare gases, the discharge machanism become similar one under the atmospheric pressure.

As has been described in detail, this invention makes unnecessary the device and equipment for the formation of vacuum systems, reduces cost, and achieves surface treatment under the atmospheric pressures, as compared with the conventional low-pressure glow discharge plasma reaction method. Since the structure and construction of the device are simple, it becomes easier to perform surface treatment of large-area substrate. The desired surface treatment can be obtainted regardless of the materials and size of the substrate.

Claims

1. An atmospheric plasma reaction method characterized by introducing a mixed gas of rare gas and reactive gas into a reaction vessel having a dielectric-coated electrode wherein the surface of two or more electrodes located parallel with each other are provided with a solid dielectrics, exciting said mixed gas of gases with plasma at atmospheric pressure, then transporting the active species to the downstream of the plasma and treating the surface of a substrate.

2. An atmospheric plasma reaction method as described in Claim 1 wherein the surface of the substrate is treated with reactive gas having halogen atoms.

3. An atmospheric plasma reaction device comprising a gas introducing means for introducing a mixed gas of rare gas and reactive gas into a reactive vessel, an atmospheric plasma generation unit wherein a dielectric-coated electrode where a solid dielectric is produced on the surfaces of two or more electrodes located parallel with each other is provided vertical to the substrate, and a surface-treatment unit for treating the surface of the substrate downstream of the plasma-generating region of the atmospheric plasma generation unit.

4. An atmospheric plasma reaction device as described in Claim 3 wherein an isolation vessel is provided to reduce the pressure to 1/10 atmospheric pressure.

FIG. 1

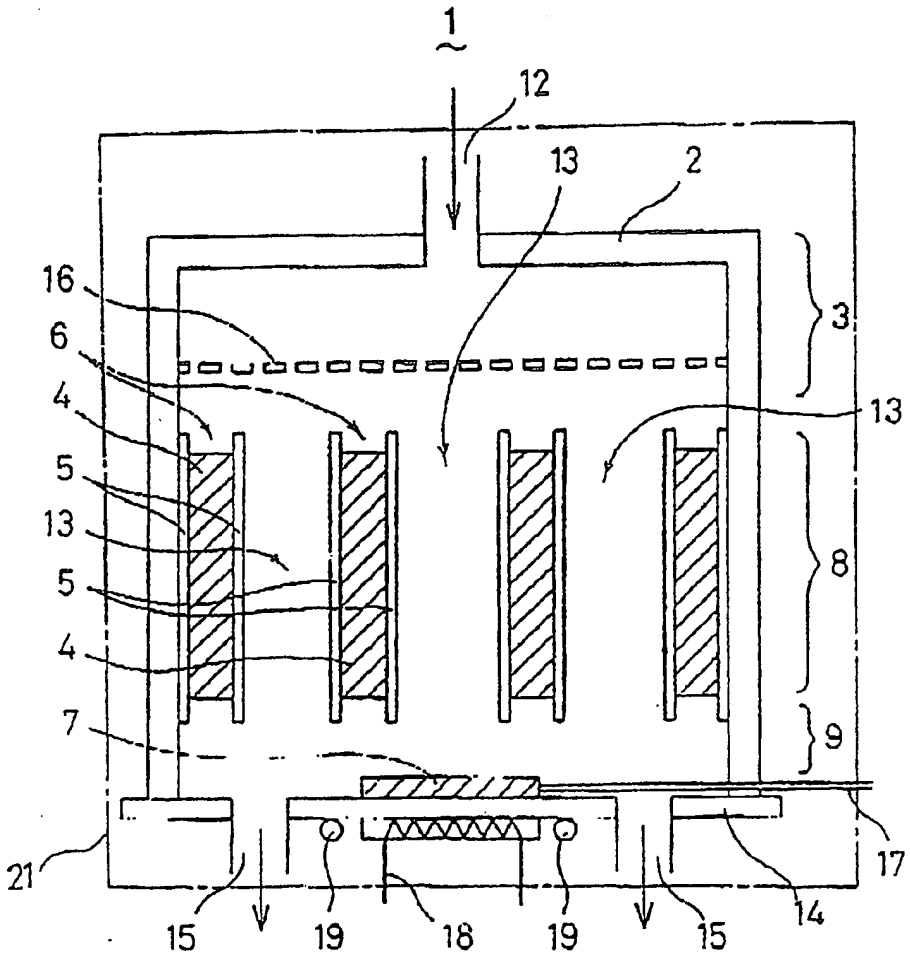


FIG. 2

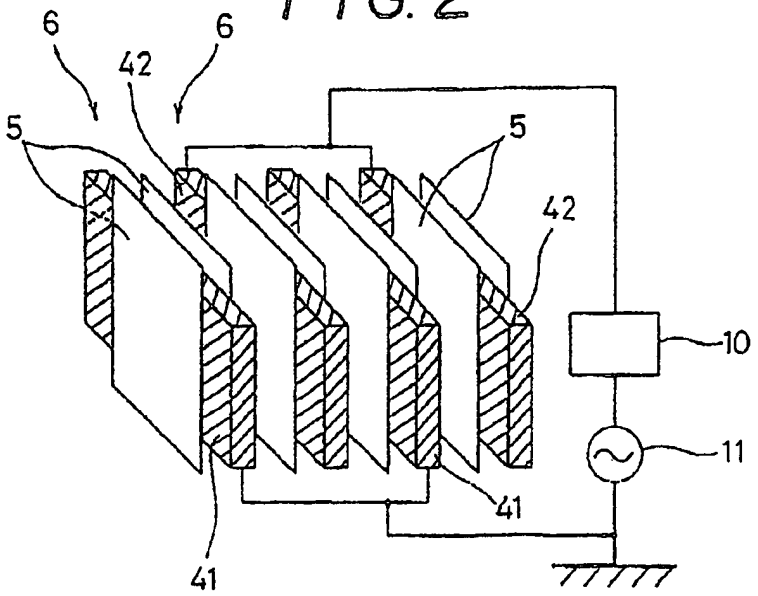


FIG. 3

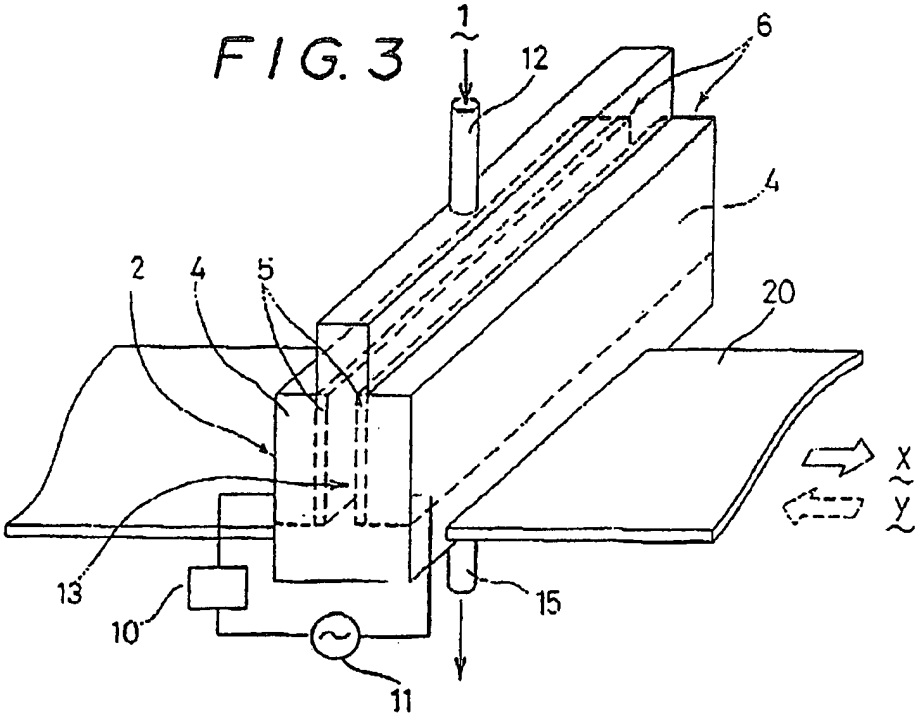


FIG. 4

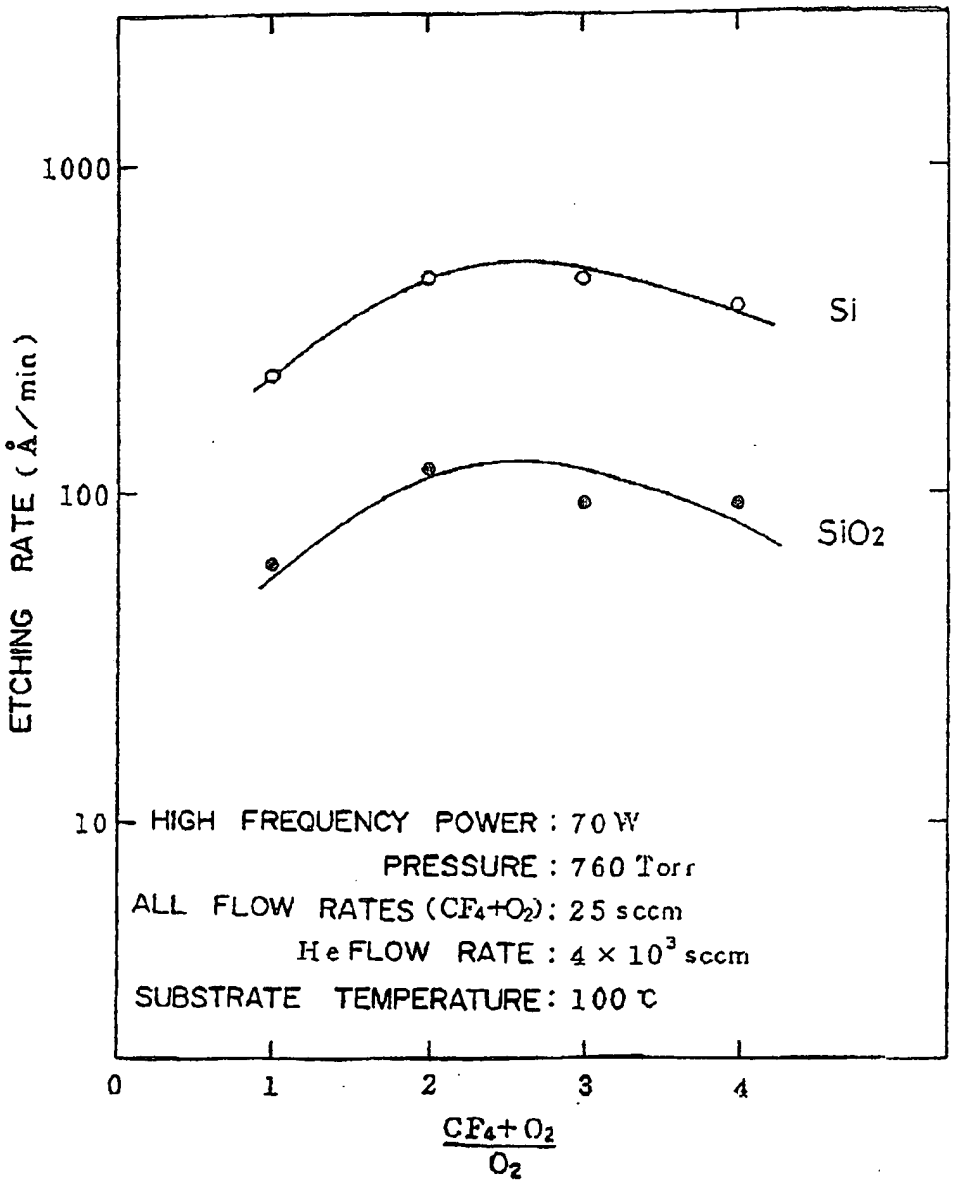

1000
100
10
ETCHING RATE (Å/min)
Si
SiO2
HIGH FREQUENCY POWER : 70 W
PRESSURE : 760 Torr
ALL FLOW RATES (CF4+O2) : 25 sccm
He FLOW RATE : 4 × 10^3 sccm
SUBSTRATE TEMPERATURE : 100 ℃
0
1
2
3
4
CF4+O2 / O2

FIG. 5

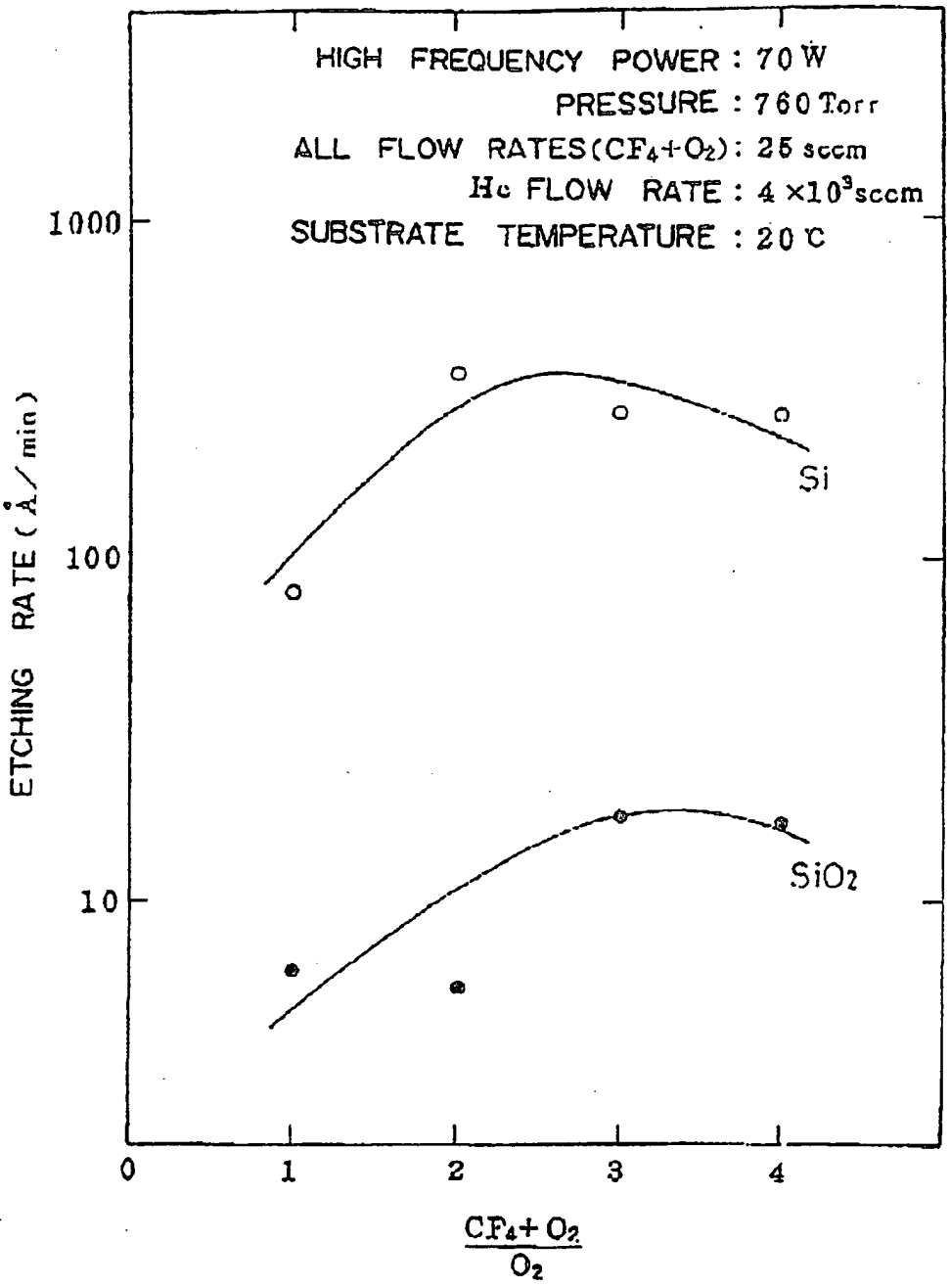

HIGH FREQUENCY POWER : 70 W
PRESSURE : 760 Torr
ALL FLOW RATES(CF_4+O_2) : 25 sccm
He FLOW RATE : 4 ×10³sccm
SUBSTRATE TEMPERATURE : 20 ℃
ETCHING RATE (Å / min)
1000
100
10
Si
SiO_2
0
1
2
3
4
$\frac{CF_4+O_2}{O_2}$

FIG. 6

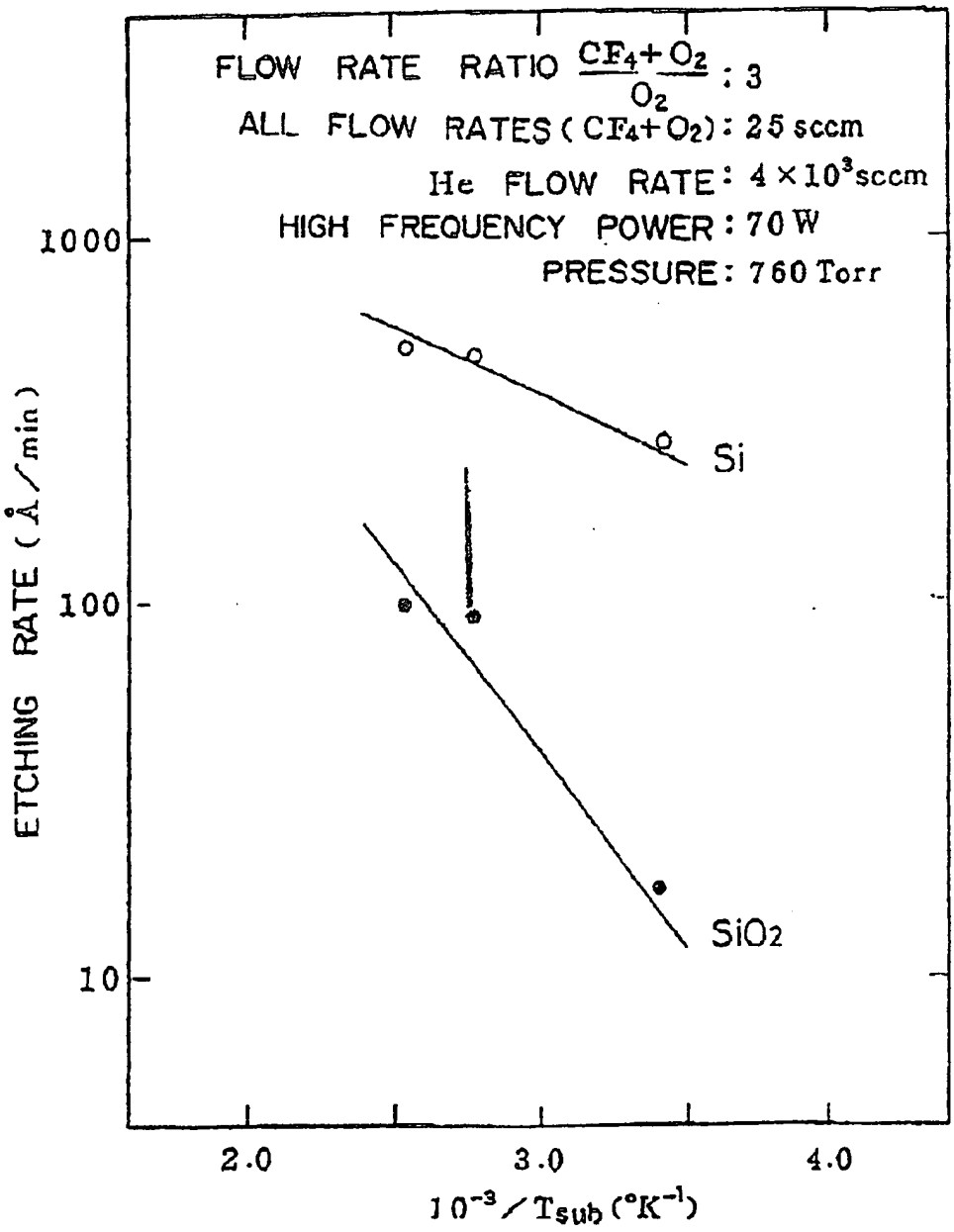
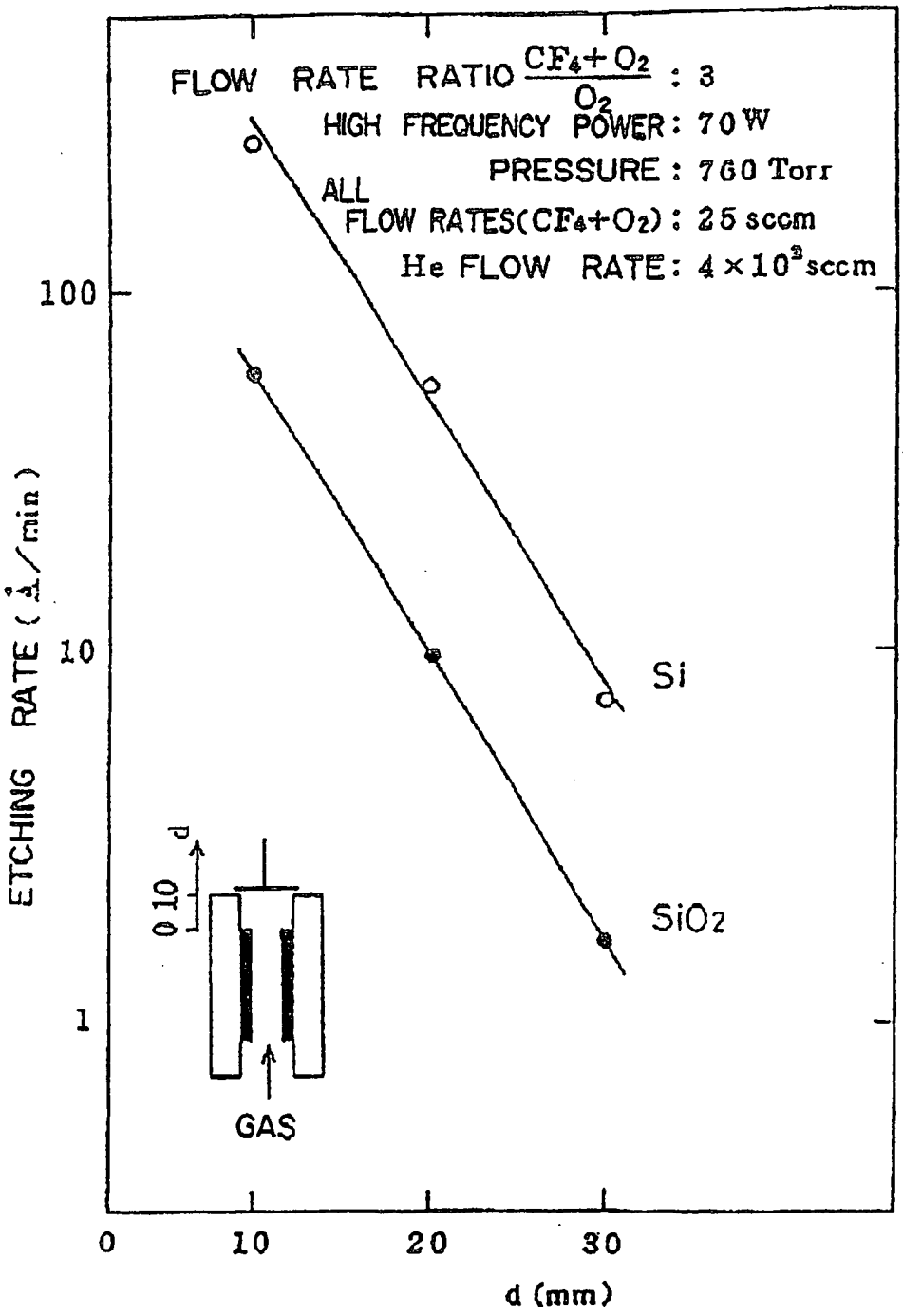

FLOW RATE RATIO $\frac{CF_4+O_2}{O_2}$: 3
ALL FLOW RATES (CF_4+O_2) : 25 sccm
He FLOW RATE : 4×10^3 sccm
HIGH FREQUENCY POWER : 70 W
PRESSURE : 760 Torr
1000
100
10
ETCHING RATE (Å / min)
Si
SiO2
2.0
3.0
4.0
10^{-3} / T_{sub} ($°K^{-1}$)

FIG. 7


FLOW RATE RATIO $\frac{CF_4+O_2}{O_2}$: 3
HIGH FREQUENCY POWER: 70 W
PRESSURE: 760 Torr
ALL FLOW RATES(CF_4+O_2): 25 sccm
He FLOW RATE: 4×10^2 sccm
ETCHING RATE (Å/min)
100
10
1
Si
SiO_2
0 10 d
GAS
0
10
20
30
d (mm)

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This invention also provides an atmospheric plasma reaction device.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 3288

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	JOURNAL OF PHYSICS D. APPLIED PHYSICS. vol. 23, nn. 8, August 14, 1990, LETCHWORTH GB pages 1125 - 1128; YOKOYAMA T ET AL.: 'The mechanism of the stabilisation of glow plasma at atmospheric pressure ' * the whole document *	1	H01J37/32
Y	JOURNAL OF PHYSICS D. APPLIED PHYSICS. vol. 21, no. 21, May 14, 1988, LETCHWORTH GB pages 838 - 840; KANAZAWA S ET AL.: 'Stable glow plasma et atmospheric pressure ' * the whole document *	1,2	
Y	PROCEEDINGS FOURTH INTERNATIONAL SYMPOSIUM ON PLASMA CHEMISTRY vol. 2, 1979, ZURICH, CH. pages 765 - 771; DONOHOE K G ET AL.: 'Plasma polymerisation of ethylene in an atmospheric pressure discharge ' * page 766, paragraph 1 2 *	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
P,Y	EP-A-346 055 (RESEARCH DEVELOPMENT CORPORATION OF JAPAN) * abstract; figures 2,10,11 * * page 3, line 27 - line 43 * * page 4, line 9 - line 26 * * page 3, line 37 - line 41 *	1,2	H01J
Y	US-A-4 554 047 (COOK ET AL.) * column 2, paragraph 2; figure * * column 4, line 10 - line 16 * * column 4, line 29 - line 40 *	1,2	
A	US-A-4 381 965 (MAHER JR. ET AL.) * figures 4,9 * * column 6, line 3 - line 30 *	1-4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 AUGUST 1991	G G COLVIN

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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